Densification Behavior and Mechanical Properties of Yttrium and Zirconium Doped Alumina Ceramics

A Project Report Submitted in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Technology
(Ceramic Engineering)

By
BHAGYAJIT DALEI
Roll No. 111cr0578

Under the supervision of
Dr. Shantanu Kumar Behera
Assistant Professor
Department of Ceramic Engineering, NIT, Rourkela

Department of Ceramic Engineering
NATIONAL INSTITUTE OF TECHNOLOGY
ROURKELA, 2015

CERTIFICATE

This is to certify that the thesis entitled, "**Densification Behavior and Mechanical Properties of Yttrium and Zirconium Doped Alumina Ceramics**" submitted by BHAGYAJIT DALEI (111CR0578) in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering session of 2014-2015 at the NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA is an authentic work carried out by him under my supervision and guidance.

I would rate this thesis as an average work for undergraduate thesis standard.

To the best of my knowledge, the matter personified in the thesis has not been submitted to any other University / Institute for the award of any Degree.

Date:

Prof. S. K. Behera
Dept. of Ceramic Engineering
National Institute Of Technology
Rourkela-769008

ACKNOWLEDGEMENT

It is with my utmost sincerity that I express my deep sense of gratitude and respect to my supervisor Prof. **Shantanu Kumar Behera** for his excellent guidance, meticulous suggestions and impeccable support throughout the project. I consider myself extremely grateful to work under the guidance of such a dynamic person. I am also thankful to Prof. **Swadesh Kumar Pratihar**, H.O.D, Department of Ceramic Engineering, NIT Rourkela for his constant support and encouragement.

Last but not the least, I extend my sincere extolment to all other faculty members, all non-teaching staff, my senior research fellowmen and friends at the Department of ceramic Engineering, NIT Rourkela, for their help and valuable advice in every stage of successful completion of this project.

Date:

BHAGYAJIT DAELI
Roll No. 111CR0578
Department of Ceramic Engineering

NIT, ROURKELA

C O N T E N T S

ABSTRACT

The densification behavior, microstructure and mechanical properties of Al_2O_3 doped with 500 ppm level of Y_2O_3 and ZrO_2 were investigated. Both of the batches were uniaxial pressed into discs and rectangular bars, and solid state-sintered at temperature of 1600 °C for 2 hrs. The density was found to increase, simultaneously with the hardness of doped composition. The Y-doped alumina body showed exaggerated grain growth while Zr-doped body resulted bimodal distribution of grains.

Keywords: **A**lumina, Zr, Y, Densification, Hardness

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Ceramics have been known to mankind since the earliest civilization and have played an important role in the evolution and development of human civilization. Generally ceramics are defined as solid crystalline materials composed of oxides, carbides, nitrides, borides having important structural, mechanical, thermal and electronic properties. Most of the ceramic materials have significant fraction of covalent bonding which ensures improved high temperature properties like high melting point, strength at high temperature etc. The improved high temperature mechanical properties, coupled with high wear, oxidation and chemical resistance makes it suitable for many advanced and strategic applications.

Alumina (Al_2O_3) is considered as one of the most vital technical ceramics. It has intrinsic features that make it a favorable candidate for wide range of application. Its electrical, mechanical, thermal and optical properties have been broadly studied because of its wide range of uses such as lasers, lamp covers, thread guides, catalytic converters and substrates for microelectronic computer chip. It can exist in many crystalline forms, among which hexagonal alpha form is stable at high temperature. This form is the strongest and stiffest of the oxide ceramics. It is found naturally as corundum in emery, topaz, amethyst, and emerald and as the priceless gemstones like ruby and sapphire, but it is also available from the more abundant ores such as bauxite, cryolite and clays that the material can be economically extracted and purified.

Corundum, with its hexagonal structure exists in rhombohedral crystals. The unit cell forms an acute rhombohedron of side length 5.2Å and plane angle of ~55°. The good mechanical and thermal properties is due to the close packing of aluminium and oxygen atoms with in the structure[1].

Profound properties of alumina are :

(a) High wear resistant

(b) Excellent dielectric properties

(c) Resistant to strong alkali and acid attack at elevated temperature

(d) Good thermal conductivily

(e) Excellent size and shape capability

(f) High strength and stiffness

(g) Available in purity range from 90% Al_2O_3 to 99.5% Al_2O_3 for the most demanding high temperature application.

1.1 Crystal Structure: Alumina is widely available in crystalline form i.e. α-aluminium oxide which is known as corundum. It has a structure of trigonal Bravaice lattice, in which each unit cell have six formula units of Al_2O_3. Each oxygen ions form a structure of hexagonal close-packed (HCP) with Al ions which fills upto two-thirds parts of the octahedral interstices.

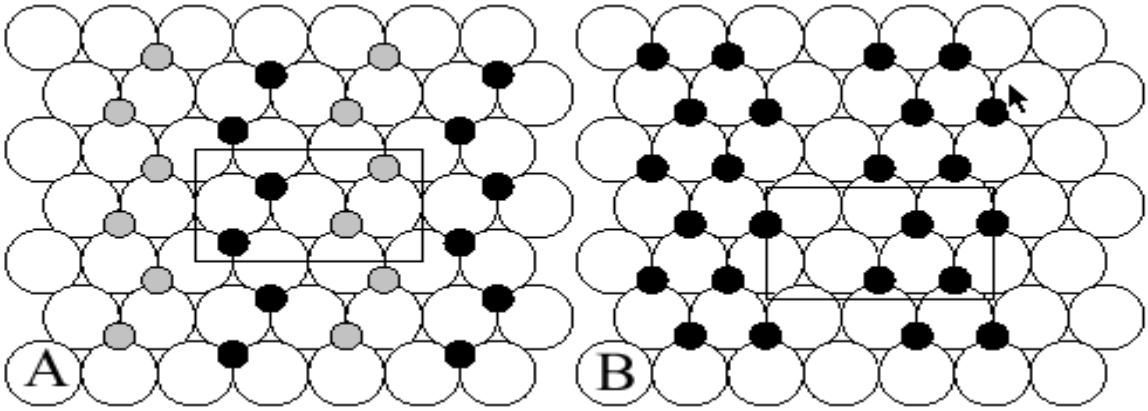


Fig1.1: Schematic drawing of the first two layers in crystal structure of Alumina (Octahedral Al ions are black, tetrahedral are grey)

1.2 Applications: Alumina ceramics have a wide range of application areas and these can be grouped as

Wear and Corrosion Resistance

The high hardness of alumina imparts wear and abrasion resistance and hence it is used in diverse applications such as wear resistant linings for pipes and vessels, pump and faucet seals, thread and wire guides etc.

Elevated Temperature and hostile Environments

The high free energy of formation of alumina makes it chemically stable and refractory, and therefore it is used as a component of hostile and elevated temperature environments.

Electrical Insulation

Alumina is act as a excellent electrical insulator due to its high electrical resistivity and dielectric strength. It is also applicable in electronics as substrates and connectors, and as spark plugs in automobiles as lower duty applications.

Biomedical

High purity alumina has been used as orthopaedic implants mainly in hip replacement surgery.

Metal Cutting Tools

The high hardness of alumina makes it applicable as the tips for metal cutting tool and abrasives.

Milling Media

Alumina is used as grinding media in a wide range of particle size reduction processes.

Chapter 2

Literature Review

In this chapter, some literature with regards to the sintering and grain growth phenomena of alumina ceramics are reviewed.

2.1 Effect of MgO addition in sintering of Al_2O_3

According to *Kingery et al* [2] addition of MgO in Al_2O_3, as a sintering aid, with a very small amount 0.25 wt% of Al_2O_3 content, allowed to achieve full density. MgO hinders the discontinuous grain growth of Al_2O_3 grains. The grain boundary do not break away from the pores which prevents the trapping of pores inside large grains, with slow/long diffusion path densification.

The mechanism by which MgO slows down grain boundary movements in alumina could be explained as:

(a) The majority of MgO doped into Al_2O_3 resides at the grain boundaries, because of very small dissolution of MgO in Al_2O_3 i.e. 300 ppm. It is because of the moderate difference in ionic radius; 0.72 Å for Mg^{2+} and 0.53 Å for Al^{3+}. (b) Any fast migration of the grain boundary would have to incorporate Mg^{2+} ions into the Al_2O_3 lattice, will the resulting increase in internal energy, unless a new compound spinel forms.

2.2 Effect of ZrO_2 addition in sintering of Al_2O_3

Wang et al [3] showed that introduction of zirconia in small amount (500-2000ppm) into alumina as a sintering aids not only helps in densification but it increases toughness. Formation of solid

solution promotes densification by introduction of lattice defects. Toughening of alumina is due to development of the partially stabilized zirconia (PSZ). Zirconia grains, as second phase, behave in intrinsic manner, i.e., it undergoes tetragonal to monoclinic transformation or retain as metastable tetragonal form by controlling cooling rate.

2.3 Effect of Y_2O_3 addition in sintering of Al_2O_3

Voytorych et al [4] made a sintering study of alumina in which silica was present as main impurity, when doped with only yttria, Yttrium is segregated at nearly at all grain boundaries. *Sato et al* [5] reflects that yttria doped in alumina gives two kind of microstructures: for finer grain sizes only segregation of yttria at grain boundaries is observed and for coarse grain sizes, the grain boundaries are saturated within yttria, which gives the inter-granular precipitation of an Yttrium rich second phase.

In yttrium co-doped alumina, the distribution of yttrium during grain growth is affected by the grain size and the total content in yttrium. Consequently, two different kinds of microstructure are observed: a microstructure with grain boundary segregation of yttrium only and a microstructure which shows both grain boundary segregation and intergranular precipitates rich in yttrium. It is shown that yttrium added to alumina in addition to magnesia does not affect grain growth; this phenomenon seems to be mainly controlled by the magnesia.

2.4 Effect of ZnO addition in sintering of alumina

It has been found that ZnO forms a spinel known as zinc alumina, $ZnAlO_4$. The chemical reaction between ZnO and alumina is occurred prior to densification of the powder compact and was accompanied by fairly large expansion. The mixing also plays a significant role the densification rate during reaction sintering and microstructure uniformity of the initial powder compacts.

2.5 Effect of La_2O_3 addition in sintering of alumina

In the experiment different amount of La_2O_3 is used as sintering aid as 0.5%, 1% and 2 wt% to find the sintering effect with respect to 0% batches of pure reactive alumina at different temperature 1550,1600 and 1650°C .It is found that La_2O_3 from cannot make any solid solution (substitutional or interstitial Solid) of Al_2O_3 and La_2O_3,which can be described by Hume Rothery rule. Since to make any solid solution the valency state should be same, electro negativity should be same ,and there should be not more than 15% in the difference of radii of ions, but here electro negativity of La and Al is different ,and also there is a large difference between the radii of La and Al. and hence they can't make solid solution.

2.6 Hume Rothary Rule: (Substitutional solid solution):

(a) Valancy should be same.

(b) Electronegativity should be similar

(c) Size difference should be within 15%.

Although valence state of Al^{3+} and Y^{3+} and electronegativity are same, but there is difference in atomic radii of Y^{3+} and Al^{3+}.

We have atomic radii of Y^{3+} and Al^{3+} as 1.06 Angstrom and 0.53 Angstrom respectively. Y substitutes Al in the lattice structure. As there is difference in size so only partial substitution takes place. Size of Y is higher than Al, so substitution causes lattice strain which leads to higher system energy hence leading to lower sintering temperature and higher density.

2.7 Summary from the literature review:

Different types and different amount of oxide additives has been used for the densification of Alumina. Various authors have discussed different properties based on their applications point of view.

2.8 Objective and Approach:

1) To study the effect of Zr doping in densification of a fine ground grade commercial alumina.
2) To study the effect of Y doping in densification of it.
3) To compare the mechanical and microstructural properties of Zr and Y doped alumina with undoped pure Alumina ceramics.

In order to obtain dense ceramics, soft chemical methods was chosen for the preparation of doped Alumina ceramics because of its good homogeneity during synthesis.

In our work we try to improve the mechanical properties of Alumina by doping different types of additives such as Zr and Y. The source of Zr was taken as zirconium isopropoxide and for yttrium it was yttrium nitrate solution. We then prepared dense pellets for different composition and did further characterization.

CHAPTER 3
MATERIALS AND METHODS

3.1 Soft chemical route

A schematic flow chart for the preparation of doped and undoped alumina ceramics has been outlined below:

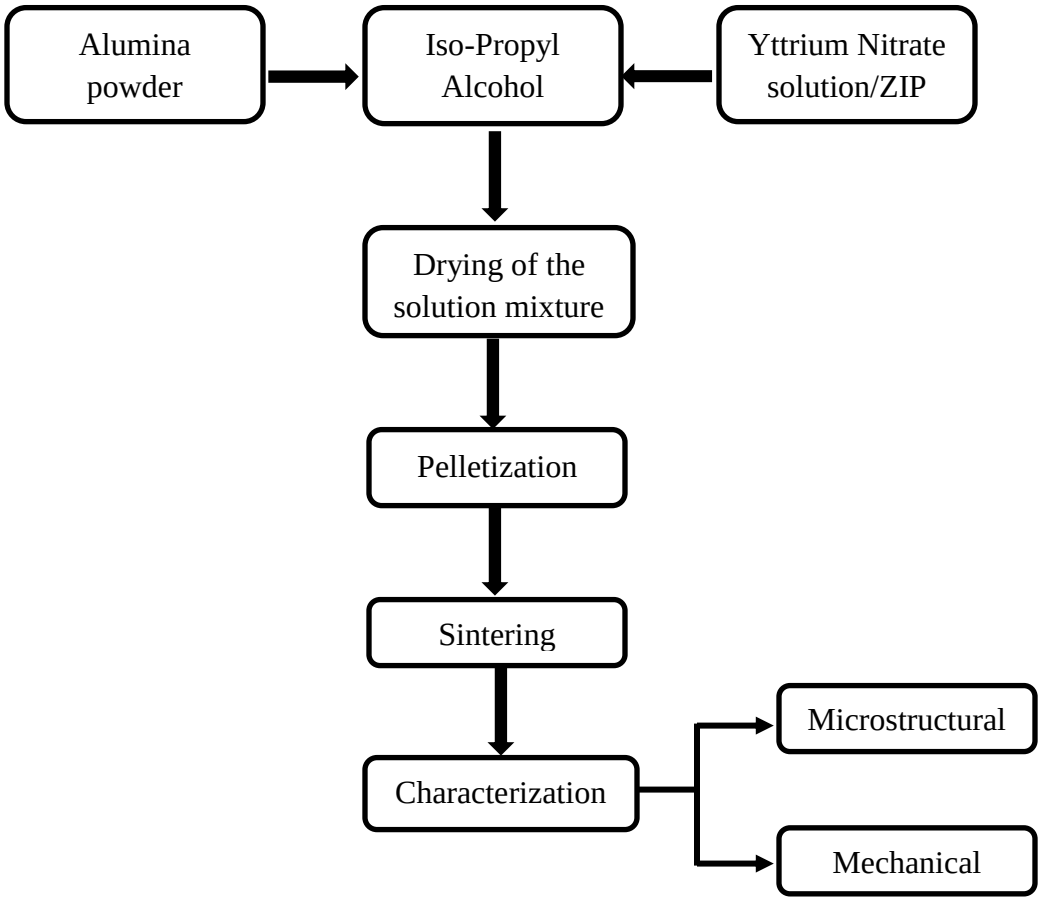


Fig: 3.1 Schematic flow chart for the preparation of undoped, Zr doped and Y doped Alumina Ceramics

Matrix Material:

Almatis Alumina A16SG, super ground graded having purity of 99.8% with rest of silica, is taken as bulk material. Undoped alumina is taken as reference sample.

Dopants:

Yttrium Nitrate and ZIP (Zirconium Iso-propoxide) are added in two different compositions at 500ppm level by soft chemical method.

For 500ppm level of Yttrium Nitrate solution and IPA(Isopropyl Alcohol) of 20ml each are mixed properly. In that solution Almatis Alumina of 10.2 g is added slowly by constant stirring.

For 500ppm level of Zirconia, ZIP of 48 micro liter is added into 20ml of IPA solution. . In that solution Almatis Alumina of 10.2 g is added slowly by constant stirring.

Both the compositions are kept inside the vacuum oven overnight for removal of IPA and then powder was obtained. Both the powder are ground into fine powder.

3.2 Compaction of pellets:

6g of Almatis alumina and other two compositions are taken, in which 1.5ml of 3wt% PVA (PolyVinyl Alcohol) is mixed as a binder.

For, 8 pellets 5.2g of powder and,1 rectangular bar 0.85g of powder from each composition is taken. For one pellet compaction 0.65g of powder is weighed.

Both the pellets and rectangular bars of each batches are pressed at load of 4.2 US Ton having dwell time of 90secs.

3.3 Drying of pellets:

After preparing the pellets, they were dried for 24 hrs at 1100°C. After drying dimensions were measured for each pellet using Vernier Callipers.

3.4 Bulk Density and Apparent Porosity of sintered pellets:

The bulk density and apparent porosity of the sintered pellets were determined by Archimedes principle using kerosene. Dry weight is measured and then the pellets were kept in kerosene, thereafter vacuum is done for about 2 hr. Then, suspended weight is measured using apparatus in which pellet is suspended in kerosene and weight is measured. After taking suspended weight, soaked weight is taken. Hence the dry weight, soaked weight and suspended weight were measured. The bulk density and apparent porosity were calculated using the formulae:

Bulk Density = dry weight / (soaked weight – suspended weight) * density of kerosene

Apparent porosity= (soaked weight-dry weight) / (soaked weight – suspended weight) *100

3.5 Dilatometric Analysis:

Dilatometry is a thermos-analytical technique used to measure the expansion or shrinkage of solids, powders, pastes and liquids under negligible load when subjected to a controlled temperature/time program. A precise understanding of this behavior can provide insight into firing processes, the influence of additives and raw materials, densification and sintering properties, reaction kinetics, phase transitions, and thermal shock.

The weight and dimensions are measured before sintering of green pellets and dilatometric analysis of rectangular bars. Dilatometric analysis of three rectangular bars of each composition are done up to temperature of 1450°C.

Six pellets, two from each composition are sintered up to 1600°C with a soaking time of 2hours.

3.6 Vickers Hardness Test:

Micro-hardness (Vickers hardness) testing of metals, ceramics, and composites is done for which 'macro' hardness measurements are unsuitable: measuring individual microstructures within a larger matrix, or measuring the hardness gradients of a part along the cross section. Micro-hardness testing gives a wide range of loads for testing with a diamond indenter; the indentation is measured as a result and converted to a hardness value. The actual indenters used are Vickers (more common; a square base diamond pyramid with an apical angle of 136°). The result for either Vickers micro-hardness is reported in GPa.

For determining the hardness of pellets, these are polished first using Emery polishing paper of grade 1/0 for 30mins, then second time polished with same paper of grade 2/0 for 20mins in order to get light reflecting surface.

Then hardness is measured using Vickers Micro-indentation machine in which load of 10kgf, with dwelling time of 10sec, is applied on the reflecting surface in five different positions. It automatically measures the hardness values, then these are converted into GPa unit and average of five values gives the hardness of that surface.

3.7 Microstructural Analysis:

In the Field Emission Scanning Electron Microscopy (FESEM), a source of electrons is focused (in vacuum) into a fine probe that is restored over the surface of the specimen. As the electrons penetrate the surface, a large number of interactions occur which can result in the emission of electrons or photons from (or through) the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors, and the output can be used to modulate the brightness

of a cathode ray tube (CRT) whose x- and y inputs are driven in synchronism with the x-y voltages restoring the electron beam. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen. Sample surfaces were polished on fine emery paper; the samples were coated for 15 min. The microstructural grain growth and densification is observed in SEM of both as-sintered surface and fracture surface.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Dilatometric analysis:

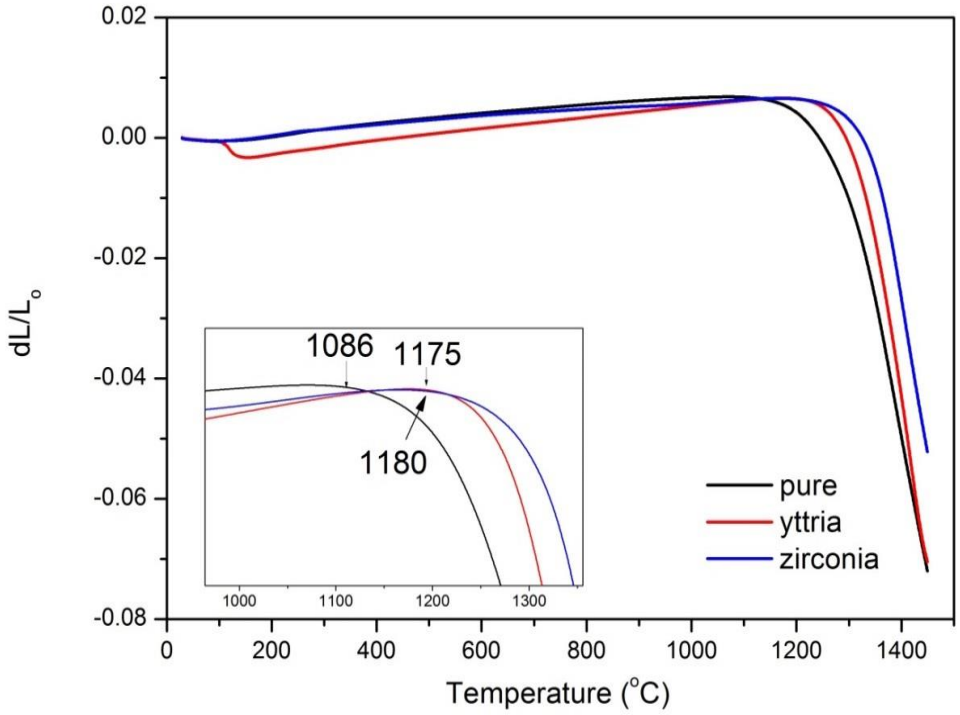


Fig: 4.1 dilatometric analysis of undoped, Zr doped and Y doped Alumina bars

Figure 4.1 shows the dilatometric curve for undoped, Zr doped and Y doped Alumina bars. The dilatometric study was carried out from room temperature to 1450^{o}C with a heating rate of 10^{o}C/min in an inert atmosphere. It was observed that around 7% linear shrinkage occurred in undoped and yttrium doped alumina bars. Thermal shrinkage of about 5% occurred for zirconia doped alumina bars. Alumina undergoes sintering around a temperature of 100°C earlier than yttrium and zirconium doped i.e. from ~1180^{o}C in doped to 1086^{o}C in undoped Alumina bars.

Also the curve shows that yttrium doped sample shows higher rate of transformation than undoped and zirconium doped sample. Based on these results, it appeared that the densification behavior of Y-doped and Zr-doped alumina is hindered by doping. However, when the sintering was carried out at 1600 °C, the results were encouraging and marginally different.

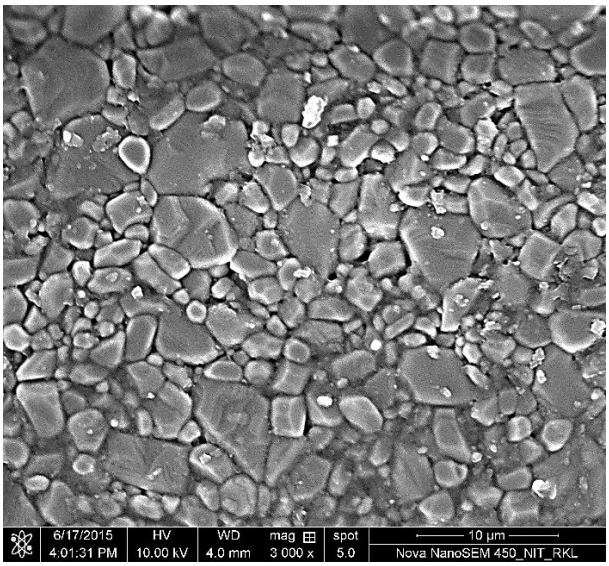
4.2 A.P, B.D and % T.D.

Composition	Bulk density (g/cc) (B.D)	Apparent porosity (A.P)in %	Theoritical density (%TD)
undoped	3.858	4.3	96.98
Yttrium doped	3.865	3.85	97.12
Zirconium doped	3.896	3.07	97.9

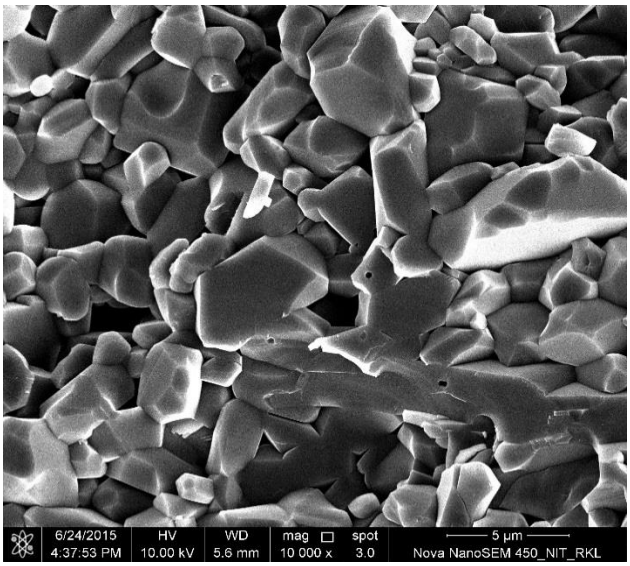
Table: 4.1 A.P. B.D. and T.D.(%) of three different composition (sintered at1600°C for 2hrs)

Table 4.1 shows the comparison of bulk density, apparent porosity and percentage of theoretical density for three different compositions. We could obtain a density of about 98% of the theoretical density in zirconium doped alumina pellets. In undoped and yttrium doped alumina pellets the density was around 97% of TD. There was a marginal increase in the density of zirconium doped pellets from undoped alumina pellets. In other words the % T.D. of yttrium doped Alumina was enhanced by 0.14% while in zirconium doped alumina pellets % T.D was enhanced by 0.95% than undoped alumina pellets.

4.3 Microstructural Analysis



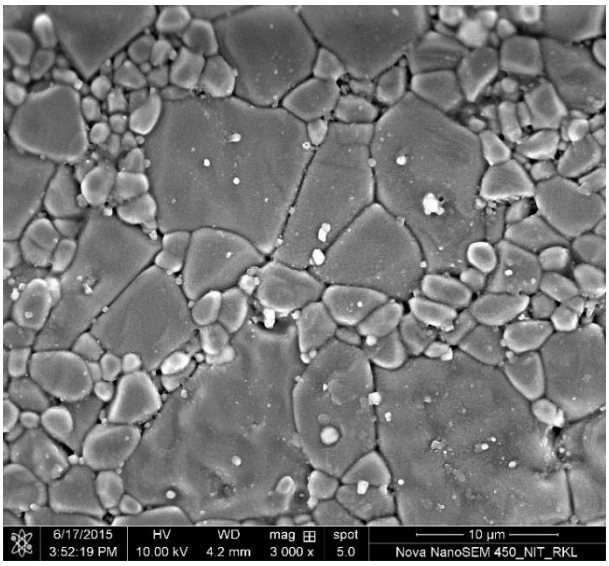
(a)

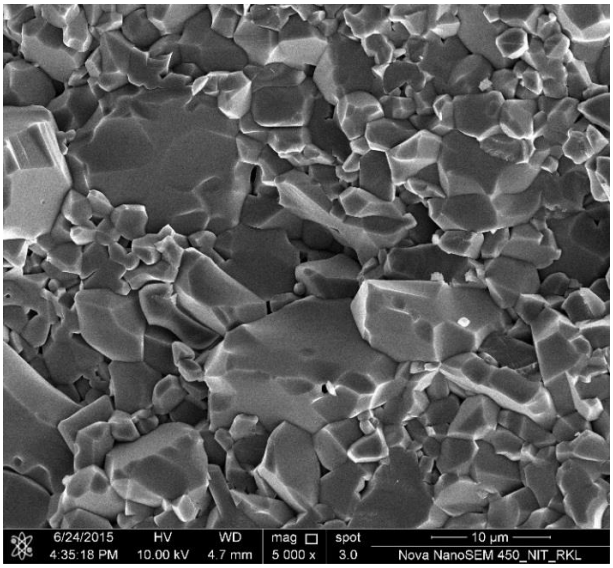


(b)

Fig 4.2 FESEM pictures of microstructural grain growth of undoped pellet sintered at 1600°C for 2hrs.

Figure 4.2 (a) showed the micrographs of the as-sintered surface of the undoped Alumina pellet sintered at 1600^{o}C for 2 hours. The grain size was in the range from 2-5 µm. There was uniform grain growth with densification in the sample. The grain boundary was clearly visible with the absence of any pores. Figure 4.2 (b) shows the fracture surface of the undoped alumina pellet sintered at 1600^{o}C for 2 hours. Figure 4.2 (b) showed the presence of negligible trapped pores outside the grains.



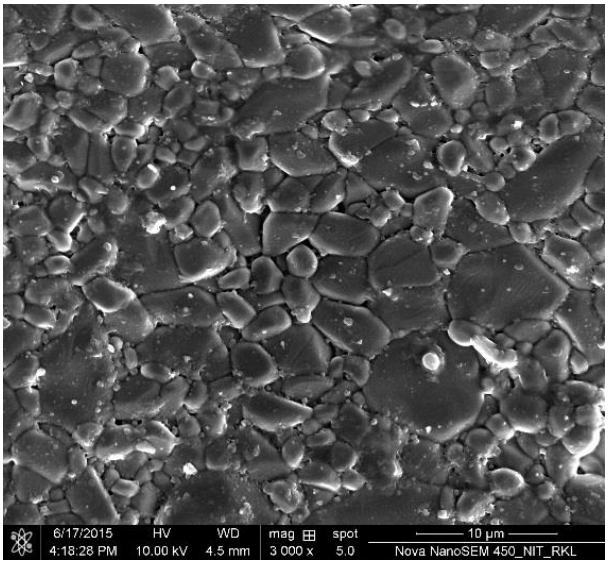


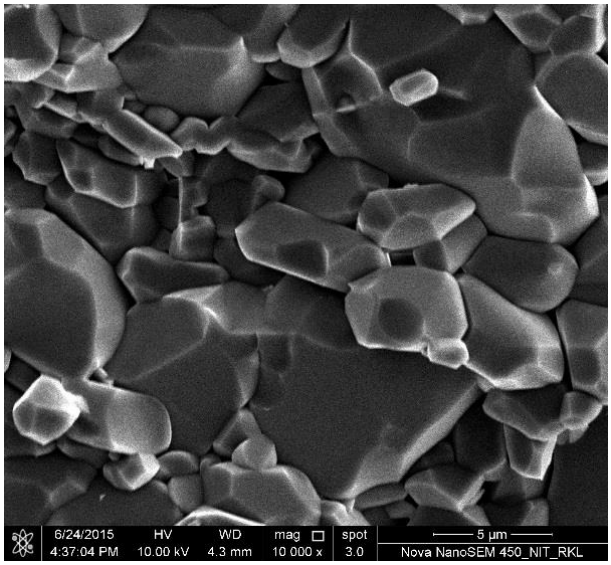
(a) **(b)**

Figure 4.3 FESEM pictures of Yttrium doped Alumina pellet (a) As-sintered surface (b) Fracture surface sintered at 1600°C for 2hrs

- Figure 4.3 (a) showed the micrographs of the as-sintered surface of the Yttrium doped Alumina pellet sintered at 1600^{o}C for 2 hours. The grain size was in the range from 2-10 µm. There was non-uniform grain growth with densification in the sample. The large difference in the size of the grain could be explained by the ostwald ripening. There were larger grains which could have grown at the expense of smaller grains. The grain boundary was clearly visible with the absence of any pores. The smaller grain are found along the boundary of larger grains. Figure 4.3 (b) showed the fracture surface of the Yttrium doped Alumina pellet sintered at 1600^{o}C for 2 hours. Figure 4.2 (b) showed the presence of negligible trapped pores inside the grains. Absence of any pores showed that the pellet were denser than undoped alumina pellets. However, it is interesting to note the growth of a few abnormal grains that occurred only with Y-doping, but not with the

undoped alumina samples. It could be ascribed to the following. The purity of the alumina powder was only 99.8%, the rest being siliceous impuriries. These impurities with the Y-based dopants produce low melting glassy composunds.





(a) **(b)**

Figure 4.4 FESEM pictures of zirconium doped Alumina pellet (a) As-sintered surface (b) Fracture surface sintered at 1600°C for 2hrs

Figure 4.4 (a) showed the micrographs of the as-sintered surface of the zirconium doped Alumina pellet sintered at 1600^{o}C for 2 hours. The grain size was in the range from 2-5 µm. There was uniform grain growth in the sample. The grain boundary was clearly visible with the absence of any pores. The difference in the sizes of largest and smallest grain was lesser than the difference in grain size of undoped alumina pellets. Figure 4.4 (b) shows the fracture surface of the zirconium doped Alumina pellet sintered at 1600^{o}C for 2 hours. Figure 4.4 (b) showed complete absence of trapped pores outside the grains which might have caused to densify the sample around 98% of TD. The Alumina pellet doped with zirconium produced highest density

which can be complimented with the microstructure evaluation. It might have happened that the Zirconium ions occuped the triple junctions and the inter-granular regions of the Alumina grains.

4.4 Vickers Micro-indentation Hardness:

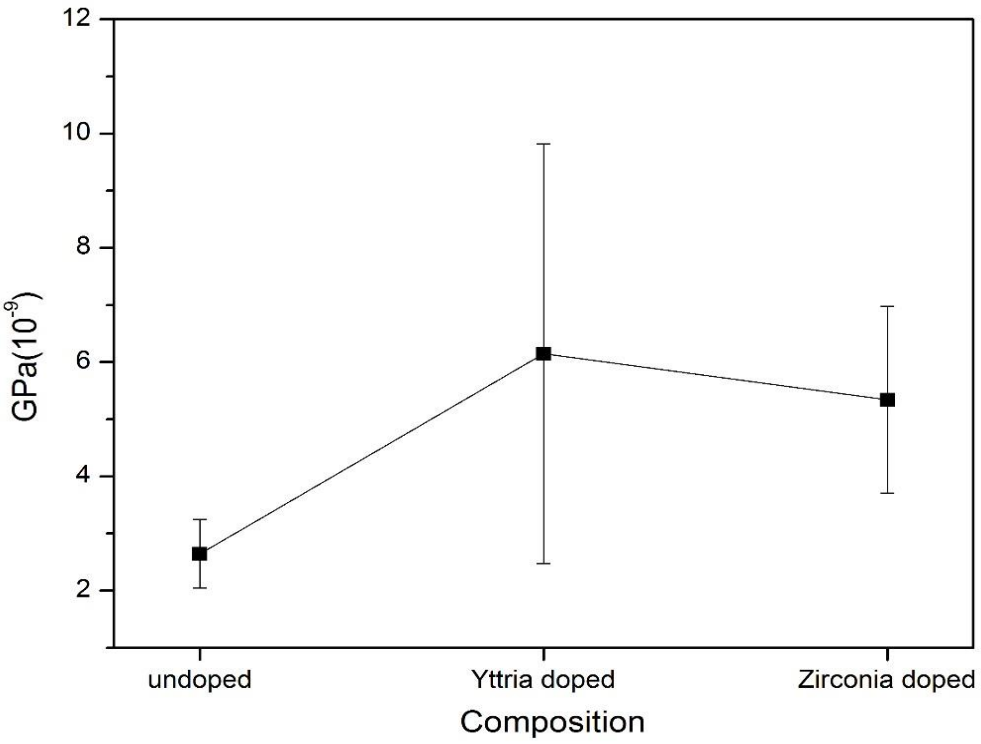


Fig 4.5: Vickers hardness at 10kgf load with dwell time of 10 secs

Figure 4.5 showed the variation of hardness in undoped and Y and Zr doped alumina pellets. The mean hardness value of yttrium doped is 6.135 GPa and that of Zirconium doped is 5.341 GPa which are higher than undoped one having value of 2.645GPa.

Presence of larger atomic sized Yttrium and Zirconium reduces the abnormal grain growth during sintering by controlling mass diffusion, hence higher densification increases hardness.

The hardness is increased due to well removal of pores from grains and interconnected pores at the grain boundary regions which is the results of sintering at 1600°C for 2hrs.

.

CHAPTER 5

CONCLUSION

5. Conclusion:

This brief study of densification behavior and mechanical properties revealed that doping yttrium or zirconium resulted in the change of microstructure and mechanical properties. The amount of dopant was intentionally kept low (500ppm) to avoid any intermediate compounds getting formed in the sample.

Doping of 500ppm of Yttrium and Zirconium in Alumina showed the following improvements:

- Doping of yttrium and zirconium in alumina marginally enhanced the densification behavior of the alumina ceramics. The effect was seen only at higher temperature; at moderate temperature the doping hindered densification.
- The abnormal grain growth in Y-doped samples were assumed to be due to the formation of various intermediate glassy compounds that enhance nonuniform grain growth.
- Zirconium doping indicated almost similar densification behavior. However, the extent of abnormal grains in this sample was lower; the grain size distribution was bimodal.

REFERENCES:

1. J.S Reed, Introduction to the Principles of Ceramic Processing, 2nd Ed., John Wiley & Sons. 1995.

2. W.D Kingery, Bowen and D.R. Uhlmann, Introduction to Ceramics, 2nd Ed. John Wiley & Sons, Singapore, 1991.

3. Wang J., Stevens R., Zirconia toughened alumina ceramics, journal of material science, 24,(1989), 1.

4. R. Voytorych, I. Maclaren, M. A. Gulgun, R. M. Carnon, M. Ruhele , Effect of yttria on densification and grain growth in α-alumina, 50,(2001), (3454).

5. Sato Eiichi and Carry Claude, Yttria doping and sintering of sub microstructure-grain α-alumina, journal of American ceramic society, 79[8],(1996), (2156).

6. P. Gruffel & C.Carry, Effect of Grain Size on Yttrium Grain Boundary Segregation in Fine-grained Alumina, Journal of the European Ceramic Society, 11, (1993), (189-199).